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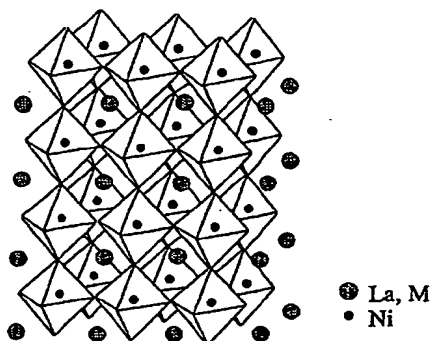
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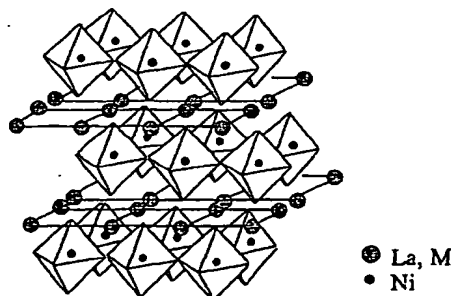
(54) **DOUBLE OXIDE WITH n TYPE THERMOELECTRIC CHARACTERISTICS**

(57) The present invention provides a complex oxide having a composition represented by the formula $\text{La}_{1-x}\text{M}_x\text{NiO}_{2.7-3.3}$ or $(\text{La}_{1-x}\text{M}_x)_2\text{NiO}_{3.6-4.4}$ (wherein M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and $0.01 \leq x \leq 0.8$), the complex oxide having a negative Seebeck coefficient at 100°C or higher. This complex oxide is a novel material which exhibits excellent properties as an n-type thermoelectric material.

Fig. 2

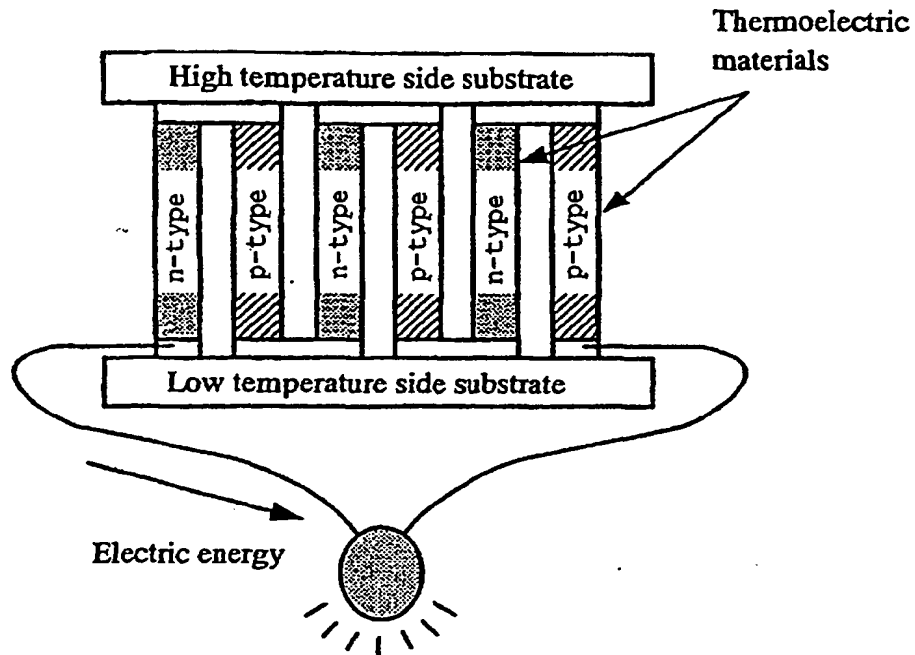


LaNiO_3 structure
(Examples 1 to 55)



La_2NiO_4 structure
(Examples 56 to 110)

Fig. 3



Description

TECHNICAL FIELD

- 5 [0001] This invention relates to a complex oxide capable of achieving high performance as an n-type thermoelectric material, and an n-type thermoelectric material using the complex oxide.

BACKGROUND ART

- 10 [0002] In Japan, only 30% of the primary energy supply is used as effective energy, with about 70% being eventually lost to the atmosphere as heat. The heat generated by combustion in industrial plants, garbage-incineration facilities or the like is lost to the atmosphere without conversion into other energy. In this way, we are wastefully discarding a vast amount of thermal energy, while acquiring only a small amount of energy by combustion of fossil fuels or other means.
- 15 [0003] To increase the proportion of energy to be utilized, the thermal energy currently lost to the atmosphere should be effectively used. For this purpose, thermoelectric conversion, which directly converts thermal energy to electrical energy, is an effective means. Thermoelectric conversion, which utilizes the Seebeck effect, is an energy conversion method for generating electricity by creating a difference in temperature between both ends of a thermoelectric material to produce a difference in electric potential. In this thermoelectric generation, electricity is generated simply by setting
- 20 one end of a thermoelectric material at a location heated to a high temperature by waste heat, and the other end in the atmosphere (room temperature) and connecting conductive wires to both ends. This method entirely eliminates the need for moving parts such as the motors or turbines generally required for power generation. As a consequence, the method is economical and can be carried out without releasing gases due to combustion. Moreover, the method can continuously generate electricity until the thermoelectric material has deteriorated.
- 25 [0004] Therefore, thermoelectric generation is expected to play a role in the resolution of future energy problems. To realize thermoelectric generation, large amounts of a thermoelectric material that has a high thermoelectric conversion efficiency and excellent heat resistance, chemical durability, etc. will be required.
- [0005] CoO_2 -based layered oxides such as $\text{Ca}_3\text{Co}_4\text{O}_9$ have been reported as substances that achieve excellent thermoelectric performance in the air at high temperatures. However, all such oxides have p-type thermoelectric properties, and are materials with a positive Seebeck coefficient, i.e., materials in which the portion located at the high-
- 30 temperature side has a low electric potential.
- [0006] To produce a thermoelectric module using thermoelectric conversion, usually not only a p-type thermoelectric material but also an n-type thermoelectric material are needed. However, n-type thermoelectric materials that have excellent heat resistance, chemical durability, etc., and have a high thermoelectric conversion efficiency have not yet been found. Therefore, thermoelectric generation using waste heat has not yet become practical.
- 35 [0007] In such circumstances, the development of n-type thermoelectric materials that are composed of abundantly available elements and have excellent heat resistance, chemical durability, etc., and have a high thermoelectric conversion efficiency is greatly desired.

40 DISCLOSURE OF THE INVENTION

- [0008] The present invention has been made to solve the above problems. A principal object of the invention is to provide a novel material that achieves excellent performance as an n-type thermoelectric material.
- 45 [0009] The present inventors conducted extensive research to achieve the above object and found that a complex oxide having a specific composition comprising La, Ni and O as essential elements and partially substituted by specific elements has a negative Seebeck coefficient and a low electrical resistivity, thus possessing excellent properties as an n-type thermoelectric material. The invention has been accomplished based on this finding.
- [0010] The present invention provides the following complex oxides and n-type thermoelectric materials using the complex oxides.

- 50 1. A complex oxide having a composition represented by the formula $\text{La}_{1-x}\text{M}_x\text{NiO}_{2.7-3.3}$ wherein M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and $0.01 \leq x \leq 0.8$, the complex oxide having a negative Seebeck coefficient at 100°C or higher.
- 55 2. A complex oxide having a composition represented by the formula $\text{La}_{1-x}\text{M}_x\text{NiO}_{2.7-3.3}$ wherein M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and $0.01 \leq x \leq 0.8$, the complex oxide having an electrical resistivity of 10 mΩcm or less at 100°C or higher.
3. A complex oxide having a composition represented by the formula $(\text{La}_{1-x}\text{M}_x)_2\text{NiO}_{3.6-4.4}$ wherein M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and $0.01 \leq x \leq 0.8$, the

complex oxide having a negative Seebeck coefficient at 100°C or higher.

4. A complex oxide having a composition represented by the formula $(La_{1-x}M_x)_2NiO_{3.6-4.4}$ wherein M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and $0.01 \leq x \leq 0.8$, the complex oxide having an electrical resistivity of 10 mΩcm or less at 100°C or higher.

5. An n-type thermoelectric material comprising the complex oxide of any one of items 1 to 4.

6. A thermoelectric module comprising the n-type thermoelectric material of item 5.

[0011] The complex oxide of the invention is an oxide whose composition is represented by the formula $La_{1-x}M_xNiO_{2.7-3.3}$ (hereinafter referred to as "complex oxide 1"), or an oxide whose composition is represented by the formula $(La_{1-x}M_x)_2NiO_{3.6-4.4}$ (hereinafter referred to as "complex oxide 2"). In complex oxides 1 and 2, M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and is a value of 0.01 or more and 0.8 or less.

[0012] Complex oxides 1 and 2 have a negative Seebeck coefficient and exhibit properties as n-type thermoelectric materials in that when a difference in temperature is created between both ends of the oxide material, the electric potential generated by the thermoelectromotive force is higher at the high-temperature side than at the low-temperature side. More specifically, complex oxides 1 and 2 have a negative Seebeck coefficient at 100°C or higher of, for example, about -1 to about -20 μV/K.

[0013] Furthermore, complex oxides 1 and 2 have good electrical conductivity and low electrical resistivity, and more specifically, an electrical resistivity of 10 mΩcm or less at 100°C or higher.

[0014] Fig. 1 shows an X-ray diffraction pattern of the complex oxide obtained in Example 1 given below, i.e., one embodiment of complex oxide 1. Fig. 1 also shows an X-ray diffraction pattern of the complex oxide obtained in Example 56 given below, i.e., one embodiment of complex oxide 2.

[0015] The X-ray diffraction patterns, although showing the presence of small amounts of impurities, clearly indicate that complex oxide 1 has a perovskite-type crystal structure and complex oxide 2 has the so-called layered perovskite-type structure, thus being a perovskite-related material.

[0016] Fig. 2 schematically shows the crystal structures of complex oxides 1 and 2. As shown in Fig. 2, complex oxide 1 has a perovskite-type $LaNiO_3$ structure in which the La sites are partially substituted by M and complex oxide 2 has a layered perovskite-type La_2NiO_4 structure in which the La sites are partially substituted by M.

[0017] Complex oxides 1 and 2 can be prepared by mixing the starting materials in such a proportion so as to have the same metal component ratio as the desired complex oxide, followed by sintering. More specifically, the starting materials are mixed to have the same La/M/Ni metal component ratio as in the formula $La_{1-x}M_xNiO_{2.7-3.3}$ or $(La_{1-x}M_x)_2NiO_{3.6-4.4}$ (wherein M and x are as defined above) and the resulting mixture is sintered to provide the desired complex oxide.

[0018] The starting materials are not particularly limited insofar as they produce oxides when sintered. Examples of usable materials include metals, oxides, compounds (such as carbonates), and the like. Examples of usable sources of La are lanthanum oxide (La_2O_3), lanthanum carbonate ($La_2(CO_3)_3$), lanthanum nitrate ($La(NO_3)_3$), lanthanum chloride ($LaCl_3$), lanthanum hydroxide ($La(OH)_3$), lanthanum alkoxides (such as dimethoxylanthanum ($La(OCH_3)_3$), diethoxylanthanum ($La(OC_2H_5)_3$) and dipropoxylanthanum ($La(OC_3H_7)_3$), and the like. Examples of usable sources of Ni are nickel oxide (NiO), nickel nitrate ($Ni(NO_3)_2$), nickel chloride ($NiCl_2$), nickel hydroxide ($Ni(OH)_2$), nickel alkoxides (such as dimethoxynickel ($Ni(OCH_3)_2$), diethoxynickel ($Ni(OC_2H_5)_2$) and dipropoxynickel ($Ni(OC_3H_7)_2$), and the like. Similarly, examples of usable sources of other elements are oxides, chlorides, carbonates, nitrates, hydroxides, alkoxides and the like. Compounds containing two or more constituent elements of the complex oxide of the invention are also usable.

[0019] The sintering temperature and sintering time are not particularly limited insofar as the desired complex oxide can be produced under such conditions. For example, the sintering may be performed at about 850°C to about 1000°C for about 20 to about 40 hours. When carbonates, organic compounds or the like are used as starting materials, the starting materials are preferably decomposed by calcination prior to sintering, and then sintered to give the desired complex oxide. For example, when carbonates are used as starting materials, they may be calcined at about 600°C to about 800°C for about 10 hours, and then sintered under the above-mentioned conditions.

[0020] Sintering means are not particularly limited and any desired means such as electric furnaces and gas furnaces may be used. Usually, sintering may be conducted in an oxidizing atmosphere such as in an oxygen stream, or in the air. When the starting materials contain a sufficient amount of oxygen, sintering in an inert atmosphere, for example, is also possible.

[0021] The amount of oxygen in a complex oxide to be produced can be controlled by adjusting the partial pressure of oxygen during sintering, sintering temperature, sintering time, etc. The higher the partial pressure of oxygen is, the higher the oxygen ratio in the above formulae can be.

[0022] The thus obtained complex oxides 1 and 2 of the invention have a negative Seebeck coefficient and a low electrical resistivity, i.e., an electrical resistivity of 10 mΩcm or less at 100°C or higher, so that the oxides exhibit

excellent thermoelectric conversion capabilities as n-type thermoelectric materials. Furthermore, the complex oxides have good heat resistance and chemical durability and are composed of low-toxicity elements and therefore highly practical as thermoelectric conversion materials.

[0023] The complex oxides 1 and 2 of the invention with the above-mentioned properties can be effectively used as n-type thermoelectric materials in air at high temperatures.

[0024] Fig. 3 is a schematic representation of a thermoelectric module produced using a thermoelectric material comprising a complex oxide of the invention as its n-type thermoelectric elements. The thermoelectric module has a similar structure to conventional thermoelectric modules and comprises a high-temperature side substrate, a low-temperature side substrate, p-type thermoelectric materials, n-type thermoelectric materials, electrodes, and conductive wires. In such a module, the complex oxide of the invention is used as an n-type thermoelectric material.

[0025] As described above, the complex oxides of the invention have a negative Seebeck coefficient and a low electrical resistivity and are also excellent in terms of heat resistance, chemical durability, etc.

[0026] The complex oxides of the invention with such properties can be effectively utilized as n-type thermoelectric materials in air at high temperatures, whereas such use is impossible with conventional intermetallic compounds. Accordingly, by incorporating the complex oxides of the invention as n-type thermoelectric elements into a thermoelectric module, it becomes possible to effectively utilize thermal energy conventionally lost to the atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] Fig. 1 shows X-ray diffraction patterns of the complex oxides obtained in Examples 1 and 56. Fig. 2 schematically shows the crystal structures of complex oxides 1 and 2. Fig. 3 is a schematic representation of a thermoelectric module comprising the complex oxide of the invention as a thermoelectric material. Fig. 4 is a graph showing the temperature dependency of the Seebeck coefficient of the sintered complex oxide prepared in Example 1. Fig. 5 is a graph showing the temperature dependency of the electrical resistivity of the sintered complex oxide prepared in Example 1.

BEST MODE FOR CARRYING OUT THE INVENTION

[0028] Examples are given below to illustrate the invention in further detail.

Example 1

[0029] Using lanthanum carbonate ($\text{La}_2(\text{CO}_3)_3$) as a source of La, nickel oxide (NiO) as a source of Ni, and potassium carbonate (K_2CO_3) as a source of K, these starting materials were well mixed in a La/Ni/K ratio (element ratio) of 0.8:1.0:0.2. The mixture was placed into an alumina crucible and calcined in the air using an electric furnace at 600°C for 10 hours to decompose the carbonates. The calcinate was milled and molded by pressing, followed by sintering in an oxygen stream at 920°C for 40 hours to prepare a complex oxide.

[0030] The complex oxide thus obtained had a composition represented by the formula $\text{La}_{0.8}\text{K}_{0.2}\text{NiO}_{3.2}$.

[0031] Fig. 4 is a graph showing the temperature dependency of the Seebeck coefficient (S) of the obtained oxide over the temperature range of 100°C to 700°C. It is apparent from Fig. 4 that the complex oxide has a negative Seebeck coefficient at 100°C or higher, thus being confirmed to be an n-type thermoelectric material in which the high-temperature side has a high electric potential.

[0032] Like Example 1, in all the Examples described below, the Seebeck coefficient at 100°C or higher was negative and showed a tendency to become more negative with a rise in temperature.

[0033] Fig. 5 is a graph showing the temperature dependency of the electrical resistivity of the complex oxide obtained in Example 1. Fig. 5 demonstrates that the complex oxide shows a low electrical resistivity, i.e., an electrical resistivity of about 10 mΩcm or less over the temperature range of 100°C to 700°C.

Examples 2-110

[0034] Starting materials were mixed in the La/M/Ni ratios (element ratios) shown in Tables 1 to 4, and the same procedure as in Example 1 was then repeated to provide complex oxides.

[0035] The starting materials were those used in Example 1 and the following materials: sodium carbonate (Na_2CO_3) was used as a source of Na, lithium carbonate (Li_2CO_3) as a source of Li, zinc oxide (ZnO) as a source of Zn, lead oxide (PbO) as a source of Pb, barium carbonate (BaCO_3) as a source of Ba, calcium carbonate (CaCO_3) as a source of Ca, aluminium oxide (Al_2O_3) as a source of Al, neodymium oxide (Nd_2O_3) as a source of Nd, bismuth oxide (Bi_2O_3) as a source of Bi, and yttrium oxide (Y_2O_3) as a source of Y.

[0036] The sintering temperature was selected from the range of 850°C to 920°C according to the desired complex

oxide.

[0037] The complex oxides obtained in Examples 1 to 55 had a perovskite-type LaNiO_3 structure in which the La sites were partially substituted by M, whereas those obtained in Examples 56 to 110 had a layered perovskite-type La_2NiO_4 structure in which the La sites were partially substituted by M.

[0038] Tables 1 to 4 below show the element ratios of the obtained complex oxides, their Seebeck coefficients at 700°C, and their electrical resistivity at 700°C.

Table 1

Formula: $\text{La}_{1-x}\text{M}_x\text{NiO}_y$				
No.	M	La:M:Ni:O	Seebeck coefficient at 700°C (μVK^{-1})	Electrical resistivity at 700°C ($\text{m}\Omega\text{cm}$)
1	K	0.8 : 0.2 : 1 : 3.2	-10	8
2	K	0.95 : 0.05 : 1 : 3.3	-8	5
3	K	0.9 : 0.1 : 1 : 3.2	-5	7
4	K	0.5 : 0.5 : 1 : 3.1	-4	4
5	K	0.2 : 0.8 : 1 : 3.3	-3	4
6	Na	0.99 : 0.01 : 1 : 3.2	-7	7
7	Na	0.95 : 0.05 : 1 : 3	-7	5
8	Na	0.9 : 0.1 : 1 : 2.9	-3	8
9	Na	0.5 : 0.5 : 1 : 3.0	-12	4
10	Na	0.2 : 0.8 : 1 : 2.8	-5	6
11	Li	0.99 : 0.01 : 1 : 3.1	-18	8
12	Li	0.95 : 0.05 : 1 : 3.2	-10	9
13	Li	0.9 : 0.1 : 1 : 2.8	-5	7
14	Li	0.5 : 0.5 : 1 : 2.7	-8	4
15	Li	0.2 : 0.8 : 1 : 3.1	-3	7
16	Zn	0.99 : 0.01 : 1 : 2.8	-7	8
17	Zn	0.95 : 0.05 : 1 : 3.2	-8	5
18	Zn	0.9 : 0.1 : 1 : 2.7	-5	6
19	Zn	0.5 : 0.5 : 1 : 3.3	-8	4
20	Zn	0.2 : 0.8 : 1 : 3.2	-3	5
21	Pb	0.99 : 0.01 : 1 : 3.0	-10	8
22	Pb	0.95 : 0.05 : 1 : 2.9	-9	5
23	Pb	0.9 : 0.1 : 1 : 3.1	-5	3
24	Pb	0.5 : 0.5 : 1 : 3.0	-7	4
25	Pb	0.2 : 0.8 : 1 : 2.8	-2	9
26	Ba	0.99 : 0.01 : 1 : 3.2	-11	8
27	Ba	0.95 : 0.05 : 1 : 3.3	-7	5
28	Ba	0.9 : 0.1 : 1 : 3.1	-5	6

Table 2

Formula: $\text{La}_{1-x}\text{M}_x\text{NiO}_y$				
No.	M	La:M:Ni:O	Seebeck coefficient at 700°C (μVK^{-1})	Electrical resistivity at 700°C ($\text{m}\Omega\text{cm}$)
29	Ba	0.5 : 0.5 : 1 : 2.8	-4	4
30	Ba	0.2 : 0.8 : 1 : 2.9	-3	3
31	Ca	0.99 : 0.01 : 1 : 3.1	-12	8
32	Ca	0.95 : 0.05 : 1 : 3.0	-8	6
33	Ca	0.9 : 0.1 : 1 : 3.3	-6	7
34	Ca	0.5 : 0.5 : 1 : 3.2	-4	4
35	Ca	0.2 : 0.8 : 1 : 2.8	-7	7
36	Al	0.99 : 0.01 : 1 : 3.2	-10	8
37	Al	0.95 : 0.05 : 1 : 2.9	-8	5
38	Al	0.9 : 0.1 : 1 : 3.1	-8	7
39	Al	0.5 : 0.5 : 1 : 3.0	-6	4
40	Al	0.2 : 0.8 : 1 : 3.3	-5	6
41	Nd	0.99 : 0.01 : 1 : 2.9	-12	8
42	Nd	0.95 : 0.05 : 1 : 2.9	-9	7
43	Nd	0.9 : 0.1 : 1 : 3.1	-5	6
44	Nd	0.5 : 0.5 : 1 : 2.8	-4	4
45	Nd	0.2 : 0.8 : 1 : 3.1	-3	4
46	Bi	0.99 : 0.01 : 1 : 3.2	-10	8
47	Bi	0.95 : 0.05 : 1 : 3.0	-8	3
48	Bi	0.9 : 0.1 : 1 : 2.8	-7	7
49	Bi	0.5 : 0.5 : 1 : 2.9	-4	5
50	Bi	0.2 : 0.8 : 1 : 3.0	-4	4
51	Y	0.99 : 0.01 : 1 : 3.2	-10	9
52	Y	0.95 : 0.05 : 1 : 3.3	-8	5
53	Y	0.9 : 0.1 : 1 : 3.2	-5	4
54	Y	0.5 : 0.5 : 1 : 3.0	-8	4
55	Y	0.2 : 0.8 : 1 : 2.8	-3	2

Table 3

Formula: $(\text{La}_{1-x}\text{M}_x)_2\text{NiO}_y$				
No.	M	La:M:Ni:O	Seebeck coefficient at 700°C (μVK^{-1})	Electrical resistivity at 700°C ($\text{m}\Omega\text{cm}$)
56	Na	1.98 : 0.02 : 1 : 3.7	-11	9
57	Na	1.9 : 0.1 : 1 : 3.9	-8	7
58	Na	1.8 : 0.2 : 1 : 3.8	-4	7
59	Na	1 : 1 : 1 : 3.8	-7	6
60	Na	0.4 : 1.6 : 1 : 4.0	-3	4

Table 3 (continued)

Formula: $(La_{1-x}M_x)_2NiO_y$				
No.	M	La:M:Ni:O	Seebeck coefficient at 700°C ($\mu V K^{-1}$)	Electrical resistivity at 700°C ($m\Omega cm$)
61	K	1.98 : 0.02 : 1 : 3.9	-9	8
62	K	1.9 : 0.1 : 1 : 4.1	-8	9
63	K	1.8 : 0.2 : 1 : 3.6	-6	7
64	K	1 : 1 : 1 : 3.7	-4	7
65	K	0.4 : 1.6 : 1 : 4.2	-5	8
66	Li	1.98 : 0.02 : 1 : 4.4	-11	8
67	Li	1.9 : 0.1 : 1 : 3.8	-8	5
68	Li	1.8 : 0.2 : 1 : 3.7	-9	7
69	Li	1 : 1 : 1 : 3.8	-4	5
70	Li	0.4 : 1.6 : 1 : 4.1	-5	4
71	Zn	1.98 : 0.02 : 1 : 4.2	-10	8
72	Zn	1.9 : 0.1 : 1 : 4.0	-7	7
73	Zn	1.8 : 0.2 : 1 : 3.9	-5	7
74	Zn	1 : 1 : 1 : 3.8	-4	4
75	Zn	0.4 : 1.6 : 1 : 4.1	-9	9
76	Pb	1.98 : 0.02 : 1 : 4.2	-10	8
77	Pb	1.9 : 0.1 : 1 : 3.7	-11	7
78	Pb	1.8 : 0.2 : 1 : 3.9	-5	7
79	Pb	1 : 1 : 1 : 3.8	-5	4
80	Pb	0.4 : 1.6 : 1 : 4.2	-3	4
81	Ba	1.98 : 0.02 : 1 : 4.3	-6	8
82	Ba	1.9 : 0.2 : 1 : 4.2	-8	6
83	Ba	1.8 : 0.2 : 1 : 4.4	-12	7

Table 4

Formula: $(La_{1-x}M_x)_2NiO_y$				
No.	M	La:M:Ni:O	Seebeck coefficient at 700°C ($\mu V K^{-1}$)	Electrical resistivity at 700°C ($m\Omega cm$)
84	Ba	1 : 1 : 1 : 3.9	-4	4
85	Ba	0.4 : 1.6 : 1 : 3.8	-16	4
86	Ca	1.98 : 0.02 : 1 : 3.9	-10	8
87	Ca	1.9 : 0.1 : 1 : 4.1	-3	9
88	Ca	1.8 : 0.2 : 1 : 4.2	-5	7
89	Ca	1 : 1 : 1 : 4.3	-7	4
90	Ca	0.4 : 1.6 : 1 : 4.0	-3	8
91	Al	1.98 : 0.02 : 1 : 3.9	-10	8
92	Al	1.9 : 0.1 : 1 : 3.8	-6	5
93	Al	1.8 : 0.2 : 1 : 4.0	-5	7

Table 4 (continued)

Formula: $(La_{1-x}M_x)_2NiO_y$				
No.	M	La:M:Ni:O	Seebeck coefficient at 700°C ($\mu V K^{-1}$)	Electrical resistivity at 700°C ($m\Omega cm$)
94	Al	1 : 1 : 1 : 4.1	-4	6
95	Al	0.4 : 1.6 : 1 : 3.8	-4	4
96	Nd	1.98 : 0.02 : 1 : 4.0	-10	8
97	Nd	1.9 : 0.1 : 1 : 3.9	-12	7
98	Nd	1.8 : 0.2 : 1 : 3.7	-5	7
99	Nd	1 : 1 : 1 : 4.2	-4	8
100	Nd	0.4 : 1.6 : 1 : 3.8	-4	4
101	Bi	1.98 : 0.02 : 1 : 4.1	-13	8
102	Bi	1.9 : 0.1 : 1 : 4.0	-4	6
103	Bi	1.8 : 0.2 : 1 : 4.2	-5	7
104	Bi	1 : 1 : 1 : 3.9	-9	8
105	Bi	0.4 : 1.6 : 1 : 4.3	-3	4
106	Y	1.98 : 0.02 : 1 : 4.0	-10	8
107	Y	1.9 : 0.1 : 1 : 4.1	-8	5
108	Y	1.8 : 0.2 : 1 : 3.9	-7	7
109	Y	1 : 1 : 1 : 4.0	-4	4
110	Y	0.4 : 1.6 : 1 : 4.1	-5	9

Claims

1. A complex oxide having a composition represented by the formula $La_{1-x}M_xNiO_{2.7-3.3}$ wherein M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and $0.01 \leq x \leq 0.8$, the complex oxide having a negative Seebeck coefficient at 100°C or higher.
2. A complex oxide having a composition represented by the formula $La_{1-x}M_xNiO_{2.7-3.3}$ wherein M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and $0.01 \leq x \leq 0.8$, the complex oxide having an electrical resistivity of 10 $m\Omega cm$ or less at 100°C or higher.
3. A complex oxide having a composition represented by the formula $(La_{1-x}M_x)_2NiO_{3.6-4.4}$ wherein M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and $0.01 \leq x \leq 0.8$, the complex oxide having a negative Seebeck coefficient at 100°C or higher.
4. A complex oxide having a composition represented by the formula $(La_{1-x}M_x)_2NiO_{3.6-4.4}$ wherein M is at least one element selected from the group consisting of Na, K, Li, Zn, Pb, Ba, Ca, Al, Nd, Bi and Y, and $0.01 \leq x \leq 0.8$, the complex oxide having an electrical resistivity of 10 $m\Omega cm$ or less at 100°C or higher.
5. An n-type thermoelectric material comprising the complex oxide of any one of claims 1 to 4.
6. A thermoelectric module comprising the n-type thermoelectric material of claim 5.

Fig. 1

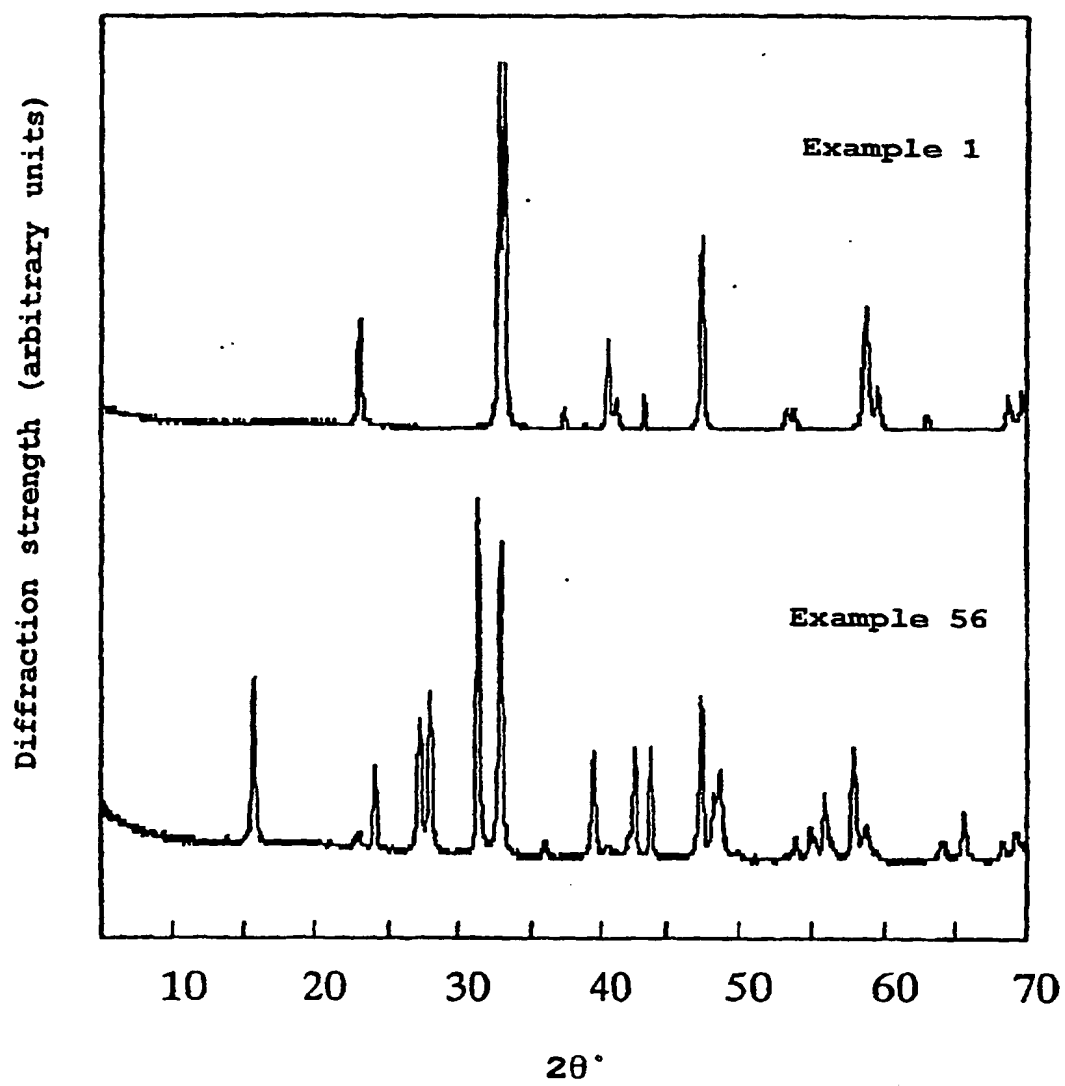
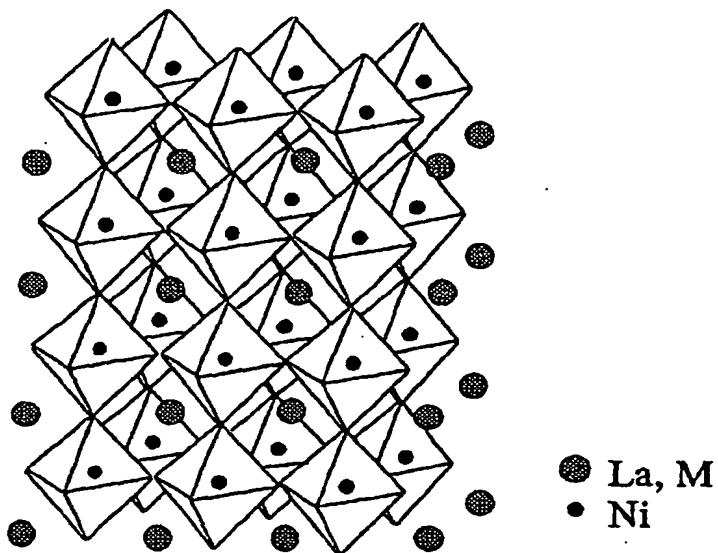
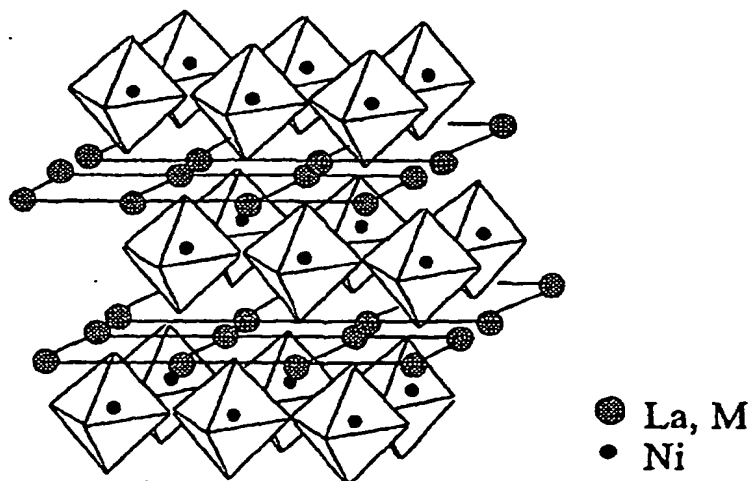


Fig. 2



LaNiO_3 structure
(Examples 1 to 55)



La_2NiO_4 structure
(Examples 56 to 110)

Fig. 3

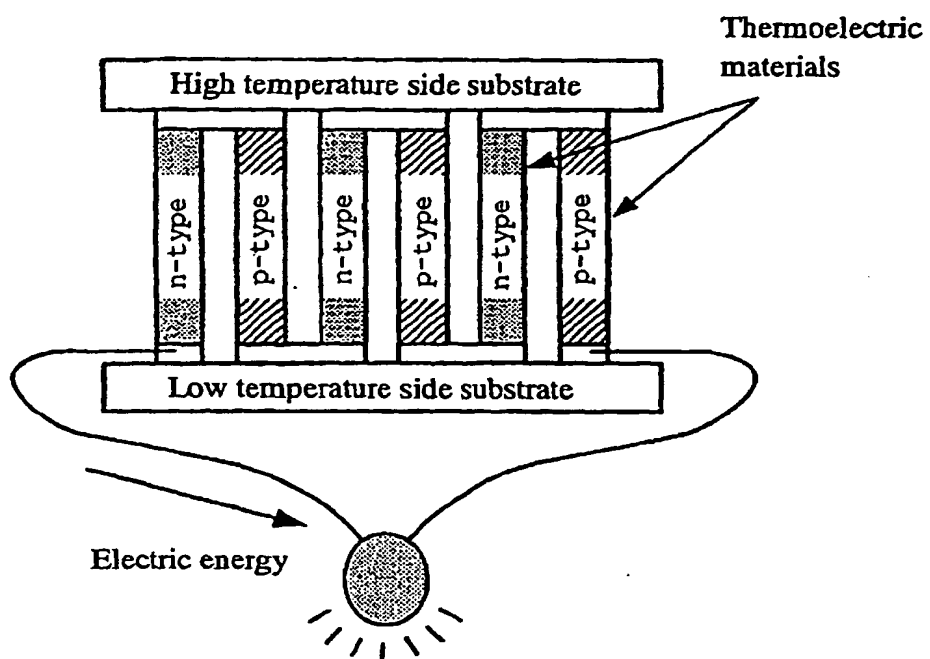


Fig. 4

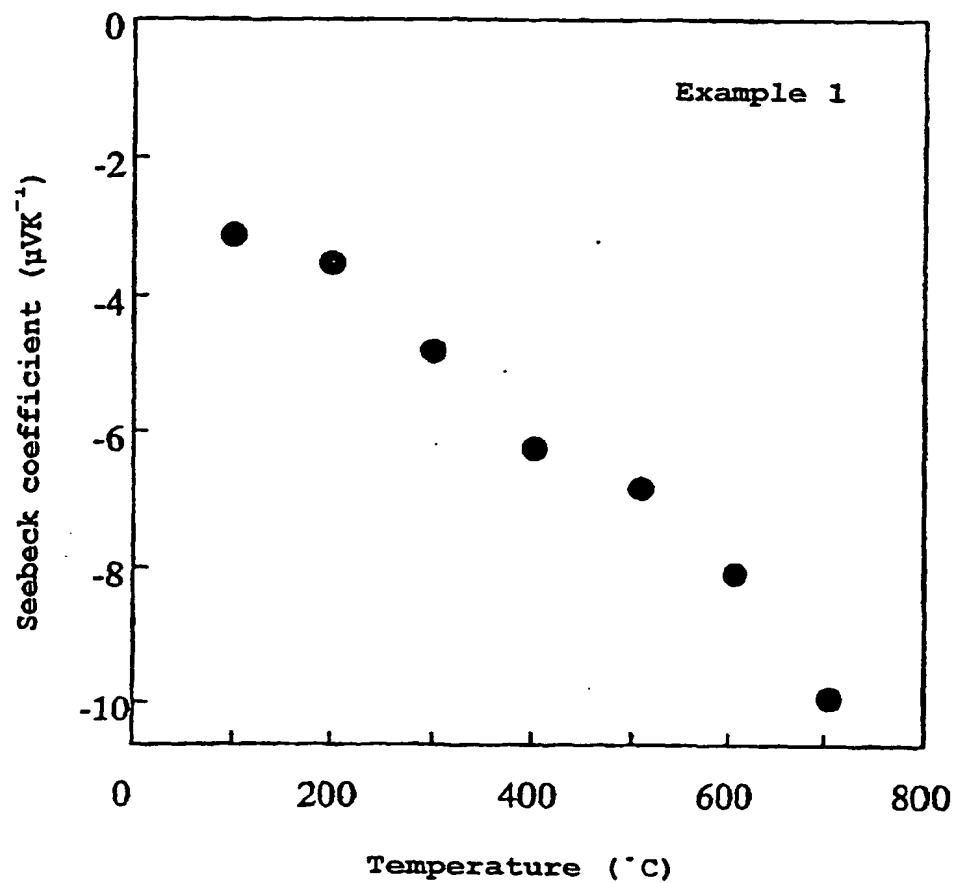
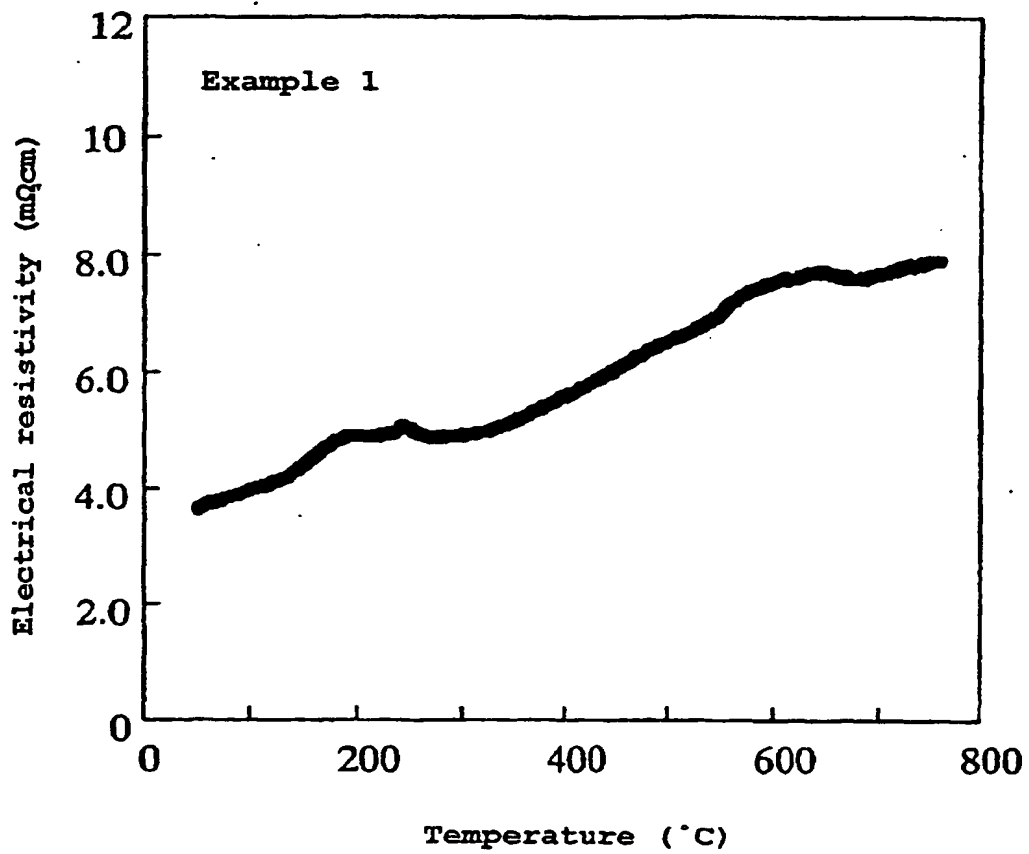


Fig. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/02827

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ H01L35/22		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ H01L35/22, B01J23/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2003 Kokai Jitsuyo Shinan Koho 1971-2003 Jitsuyo Shinan Toroku Koho 1996-2003		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2000-211971 A (Toyota Central Research And Development Laboratories, Inc.), 02 August, 2000 (02.08.00), Full text; Figs. 1 to 4 (Family: none)	1-6
A	US 2001/0016554 A1 (TOYOTA JIDOSHA KABUSHIKI KAISHA), 23 August, 2001 (23.08.01), Full text; Figs. 1 to 5 & JP 2001-269578 A & EP 1118375 A2	1-6
A	JP 8-229355 A (Nissan Motor Co., Ltd.), 10 September, 1996 (10.09.96), Full text (Family: none)	1-6
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search 28 May, 2003 (28.05.03)		Date of mailing of the international search report 10 June, 2003 (10.06.03)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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